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A STUDY OF THE PEARCE-LOW METHOD FOR THE DETERMINATION OF TIN IN ORES

BY

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A THESIS SUBMITTED FOR THE DEGREE OF MASTER OF SCIENCE

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OUTLINE OF THESIS.

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IV. SUMMARY.

A STUDY OF THE PEARCE-LOW METHOD FOR THE DETERMINATION OF TIN IN ORES.

I. INTRODUCTION. Many methods have been suggested for the determination of tin in ores. Among the gravimetric methods are the potassium cyanide, the sulphur-sodium carbonate fusion and the electrolytic methods. In the potassium cyanide method the purified ore is fused with potassium cyanide forming a button of tin, which is weighed. The sulphur-sodium carbonate fusion changes the tin to soluble sodium sulpho-stannate, from which it is precipitated by acidulation with hydrochloric acid and weighed as stannic oxide. Tin is determined electrolytically by depositing from the hot oxalate solution acidified with oxalic acid.

The volumetric methods depend on the oxidation of solutions of stannous chloride. These solutions are made by reducing the ore with hydrogen and dissolving the metal in hydrochloric acid, or by reducing stannic solutions. The stannic solutions are usually obtained from the ore by fusion with sodium hydroxide, forming sodium stannate which is dissolved in dilute hydrochloric acid. The acid stannic solutions are then reduced with zinc, iron, nickel or antimony and the amount of stannous tin determined in one of

the following ways,-

(1) Indirectly, by adding excess of ferric chloride and titrating the resulting ferrous chloride with potassium permanganate or potassium dichromate.

(2) Directly, (a) by titration with standard ferric chloride solution,

(b) by titration with iodine in alkaline solution , or

(c) by titration with iodine in acid solution.

Among the most used of these methods is the volumetric method of Pearce and Low. This method determines the tin directly by titration with iodine and is, without question, a short and easy method. The work which follows is a study of the accuracy of this method.

II. COMPARISON WITH THE ROSE GRAVIMETRIC METHOD.

The Pearce-Low method was checked on pure stannic oxide by means of the Rose sulphur-fusion method. The stannic oxide was kept in a desiccator and samples for analysis by these methods were weighed alternately in order to minimize any effect due to absorption of moisture from the atmosphere.

1. Analyses by the Rose method. The samples of stannic oxide analyzed by this method were weighed into porcelain crucibles and fused for one and one half hours with a mixture of equal parts of sulphur and sodium carbonate. After

cooling the fusions were dissolved in warm water. The solutions containing the tin as sodium sulphostannate were filtered and the slight residues washed with dilute ammonium sulphide solution. The tin was then precipitated as sulphide by acidulation with hydrochloric acid. The tin sulphide precipitates were washed by decantation with slightly acid dilute ammonium acetate solution, transferred to the filter papers and the washing continued until free from chlorine. The precipitates were dried at 110 degrees. Then the filter papers were ignited separately in porcelain crucibles and the tin sulphides added. The ignition was continued at a low temperature until all sulphur fumes were removed. The heat was then increased and finally the stannic oxide residues were heated to constant weight with Scimatco burners. Table I gives the data and results of these determinations.

2. Pearce-Low method,(a) Analyses of stannic oxide. The samples of stannic oxide analyzed by the Pearce-Low method were treated as follows. Ten grams of sodium hydroxide were fused in an iron crucible, the fusion cooled and the stannic oxide weighed into the crucible. The crucible was covered and heated to quiet fusion at a low red heat 45-60 minutes. The fusion was then poured into a clean iron dish floating on water. The hot crucible and lid used in the fusion were placed in a casserole containing a small amount of water

and the adhering fusion dissolved by heating. The crucible and lid were then rinsed with water and removed. The cake was removed from the dish and placed into the casserole. Any of the fusion sticking to the dish was removed with dilute hydrochloric acid and added to the tin solution. Thirty cc of strong hydrochloric acid were added and the casserole heated to boiling. When the cake had dissolved the solution was transferred to a 600 cc wide mouthed Erlenmeyer flask, 50 cc of strong hydrochloric acid were added and the solution diluted to 200 cc with hot water. A coil of pure sheet nickel with a surface of 12 square inches was added, the solution heated to near boiling and a rapid evolution of hydrogen maintained for 60 minutes. A piece of marble was then added and the flask cooled to room temperature. When cold the nickel coil was removed by means of a nickel wire and washed with cold boiled water containing approximately the same percent of acid as the tin solution in the flask. Starch paste was added and the standard iodine solution introduced rapidly until the blue color appeared. The evolution of carbon dioxide from marble in the flask was continued during the titration, which was carried out with the tip of the burette deep in the flask and the flask covered as much as possible with a watch glass. The results obtained by this method are given in Table II.

(b) Standardization of iodine. The iodine solutions were standardized as follows. A 250 cc Erlenmeyer flask was fitted with a two holed rubber stopper and connected with a carbon dioxide generator. Two tenths of a gram of pure tin foil was placed in the flask and a stream of dry carbon dioxide passed through to expel the air. Then 20 cc of concentrated hydrochloric acid was added through a separatory funnel and the tin dissolved by warming. The stream of carbon dioxide was continued throughout the preparation, cooling and titration of the stannous chloride solution. The titration was carried out with the tip of the burette through one hole of the rubber stopper. The iodine solutions standardized in this way checked as well as when standardized in the usual way with arsenious acid and gave a slightly larger tin factor.

The five determinations by the sulphur-fusion method average 78.74 percent for the amount of tin in the stannic oxide. This average is .07 of a percent below the theoretical amount and the analyses check within .3 of a percent. (See Table I.) Seven analyses by the Pearce-Low method average 74.99 percent for the tin in the stannic oxide. This average is 3.8 percent below the theoretical amount and the different determinations do not check well.(See Table II.) From these results it appears that the Pearce-Low method fails to give the entire amount of tin in the stannic oxide.

TABLE I.

Stannic oxide by the sulphur-fusion method.

No.	SnO_2 used.	SnO_2 found.	Tin found.	Error.
1	.1867 gram	.1860 gram	.1466 gram	-.0005 gram
2	.1663 "	.1661 "	.1309 "	-.0002 "
3	.1230 "	.1230 "	.0969 "	.0000 "
4	.1688 "	.1689 "	.1338 "	+.0008 "
5	.1611 "	.1611 "	.1269 "	.0000 "

TABLE II.

Stannic oxide by the Pearce-Low method.

No.	SnO_2 used.	Tin found.	Error.
1	.1301 gram	.0934 gram	-.0091 gram
2	.4589 "	.3437 "	-.0179 "
3	.4073 "	.3066 "	-.0143 "
4	.1518 "	.1144 "	-.0052 "
5	.1756 "	.1320 "	-.0063 "
6	.1707 "	.1301 "	-.0044 "
7	.1626 "	.1239 "	-.0042 "

III. TESTS ON THE PEARCE-LOW METHOD.

1. Test for completeness of solubility of ore. Six analyses of stannic oxide were made by the Pearce-Low method to determine whether or not the low percentages of tin were caused by incomplete solution of the stannic oxide. In these analyses the slightly acid sodium sulphostannate solutions were filtered and the amount of tin in the residues determined by a second fusion with sodium hydroxide. Table III shews the number of cubic centimeters of iodine solution required for the first fusion, the number of cubic centimeters of iodine solution required for the second fusion and the total percent of tin after deducting a blank of .1 cc of iodine. These analyses show that the residues did not contain undissolved stannic oxide, except in two cases and in these the small amounts did not materially increase the amount of tin. The low percentages of tin given by the Pearce-Low method cannot be caused by incomplete solution of the tin oxide. (Data page 8 Table III.)

2. Tests for completeness of reduction with iron, nickel and antimony. For these tests a solution of stannic chloride was made in the following way. Four grams of pure tin foil were dissolved in 50 cc of concentrated hydrochloric acid at a temperature below 25 degrees. The solution was then oxidized to stannic chloride with potassium chlorate

TABLE III.

1. Test for completeness of solubility of stannic oxide.

	Iodine used.			
SnO_2 used.	1st fusion.	2nd fusion.	Tin found.	Error.
.1732 gram	20.35 cc	.15 cc	.1039 gram	-.0325 gram
.2131 "	29.00 "	.75 "	.1513 "	-.0166 "
.1038 "	15.00 "	.30 "	.0813 "	-.0044 "
.2023 "	26.40 "	.10 "	.1346 "	-.0242 "
.1538 "	20,40 "	.10 "	.1040 "	-.0172 "
.2300 "	34.60 "	.10 "	.1766 "	-.0046 "
Blank	.10 "	.10 "	.00054 "	

and the slight excess of chlorine removed by addition of ammonium chloride. The stannic solution was made up to a liter with water and 50 cc portions were measured out by a burette into wide mouthed Erlenmeyer flasks for reduction. Enough concentrated hydrochloric acid to make a total of 50 cc was added to each flask and then enough hot water to make a total volume of 200 cc. Reductions of these acidified stannic solutions were made with iron, nickel and antimony. The reductions with iron and nickel were carried out as described in the Pearce-Low method. The iron reductions were made with coils of wrought iron and the antimony reductions with powdered antimony, which was not removed during titration. The cooling and titrating were both carried out in an atmosphere of carbon dioxide produced by marble in the flask. The iodine solution was standardized as previously described and the tin foil used in the standardization was the same as that used in making the stannic solution. Results obtained by these reductions for different lengths of time are given in Table IV.

The amount of tin found by both the iron and nickel reductions increases with the time of reduction and for the longest reductions is more than one percent below the actual amount of tin. A more complete reduction is impossible because the color of the iron and nickel chloride produced

in reductions for longer than 60 minutes, seriously interferes with the color of the end point. That these low results are not due to incomplete reduction is shown later by the results of tests with the atmospheric oxidation eliminated. (Table IX. page 22.) The percentages of tin in the antimony reductions are one and one half percent higher than the actual amount of tin. These results do not check well and do not appear to be more reliable than the the results with the iron and nickel reductions.

TABLE IV.

Tests for completeness of reduction.

Weight of tin in each sample .2 gram. Acid concentration 50 cc concentrated HCl in a total volume of 200 cc.

(a) Reductions with iron for 30, 45 and 60 minutes.

30 min.		45 min.		60 min.	
Tin found.	Error.	Tin found.	Error.	Tin found.	Error.
.1956 gram	-.0044	.1958 gram	-.0042	.1985 gram	-.0015
.1948 "	-.0052	.1976 "	-.0024	.1980 "	-.0020
.1961 "	-.0039	.1958 "	-.0042	.1993 "	-.0007
.1942 "	-.0058	.1978 "	-.0022	.1951 "	-.0049
.0007 Blank		.0007 Blank		.0007 Blank	
.1952 "	-.0048	.1968 "	-.0032	.1977 "	-.0023

(The numbers below the lines are averages.)

(Table IV continued.)

(b) Reductions with nickel for 30, 45 and 60 minutes.

30 min.		45 min.		60 min.	
Tin found.	Error.	Tin found.	Error.	Tin found.	Error.
.1916 gram	-.0084	.1968 gram	-.0032	.1979 gram	-.0021
.1361 "	-.0639	.1927 "	-.0073	.1972 "	-.0028
.1682 "	-.0318	.1956 "	-.0044	.1960 "	-.0040
.1822 "	-.0178	.1951 "	-.0049	.1949 "	-.0051
.0005 Blank	______	.0006 Blank	______	.1947 "	-.0053
.1695 "	-.0305	.1951 "	-.0049	.0009 Blank	______
				.1961 "	-.0039

(Numbers below the lines are averages.)

(c) Reductions with antimony for 10 minutes.

	Tin found.	Error.	
	.2030 gram	+.0030 gram	
	.2023 "	+.0023 "	
	.2004 "	+.0004 "	
	.2027 "	+.0027 "	
	.2013 "	+.0013 "	
	.2090 "	+.0090 "	
	.2044 "	+.0044 "	
	.1968 "	-.0032 "	
	.1952 "	-.0048 "	Blank .0014 gm
Average-	.2023 "	+.0033 "	

3. Test for deposit of tin on the reduction coils.

Tests were made to determine whether or not the low results by the Pearce-Low method were caused by separation of metallic tin on the coils used in the reduction. Some of the coils were blackened during the reduction. Such coils were warmed in concentrated hydrochloric acid and the solution tested for stannous chloride with ammonium molybdate solution. No trace of tin was found, and the black when rubbed off from the coils and tested in this way did not show a trace of tin. When the black coating of the coils was treated with concentrated nitric acid it did not show any evidence of the formation of metastannic acid and did not leave a residue on ignition. This black coating was also produced in the reduction of the blank samples and appeared to come from carbon impurities in the coils. The low results of the Pearce- Low method can not be caused by the separation of tin on the coils used in reduction.

4. Test for volatility of tin as stannic chloride.

Tests were made with the Pearce-Low method to determine whether or not any tin volatilized as stannic chloride. Samples of stannic oxide were analyzed in the usual way, but with the apparatus arranged so as to condense any volatile stannic chloride. A 500 cc Erlenmeyer flask was connected with a second flask by means of a delivery tube which

le~~a~~d into concentrated hydrochloric acid in the second flask. A portion of the tube between the flasks was cooled with a jacket of ice water and any substance distilling from the first flask was condensed and collected in the acid solution of the second flask. The sodium hydroxide fusion of the stannic oxide was neutralized and acidified in the first flask by adding hydrochloric acid through a separatory funnel. The reduction of the stannic solution with nickel coils and the cooling of the stannous solution with the evolution of carbon dioxide from marble were also carried out with the flasks connected as described. After titrating the stannous chloride in the first flask the solution in the second flask was reduced with nickel, cooled and titrated in the usual way. The amounts of tin found in this way are as follows,-

SnO_2 used.	Iodine required.		Tin found.	Error.
	1 st flask.	2 nd flask.		
.1592 gram	23.20 cc	.15 cc	.1255 gram	-.0337
.1999 "	28.05 "	.15 "	.1575 "	-.0424
.1635 "	24.30 "	.10 "	.1288 "	-.0347
Blank	.10 "	.10 "	.00053 "	

These results show that no appreciable amount of tin was lost from the first flask by volatilization and that the low results of the Pearce-Low method can not be accounted for in this way.

5. Tests for the oxidation of stannous chloride by air.

Tests were made on the titration of stannous chloride with iodine in order to determine the extent of atmospheric oxidation, the influence of acid concentration on such oxidation and the efficiency of carbon dioxide in preventing this oxidation. The tin solutions used in the tests were made by dissolving two tenths gram portions of tin in hydrochloric acid, then adding sufficient acid to make the desired concentration and enough hot water to make a total volume of 200 cc. Such solutions contained about 90 percent of the tin in the stannous condition. These solutions were reduced with nickel coils for intervals of 15 and 30 minutes and then cooled and titrated as described in the Pearce-Low method. One half of the titrations were made without the addition of marble for the evolution of carbon dioxide during cooling and titration. The acid concentrations used were 20, 50 and 80 cc of hydrochloric acid (Density 1.2) in a total volume of 200 cc. Complete data and results of these tests are given in Tables V, VI, VII and VIII.

From a summary of the results of these titrations (Table VIII.) it appears that the stannous chloride solutions were oxidized by the air to the extent of .2 to 1.7 percent when the evolution of carbon dioxide was omitted in the cooling and titration, and that this oxidation increased

with the acid concentration in both the titrations in air and carbon dioxide. The evolution of carbon dioxide from marble in the flasks did not seem to prevent all the oxidation by air since none of the amounts of tin obtained are as high as the actual amount of tin used.

DATA FOR TESTS OF OXIDATION OF STANNOUS CHLORIDE BY AIR.

Weight of tin in all samples .2 gram.

Reductions all made with nickel coils.

Total volume of solutions 200 cc.

TABLE V.

Amount of hydrochloric acid in each sample 20 cc.

(a) Titrations in air.

Reduced 15 min.		Reduced 30 min.	
Tin found.	Error.	Tin found.	Error.
.1947 gram	-.0053 gram	.1957 gram	-.0043 gram
.1970 "	-.0030 "	.1980 "	-.0020 "
.1970 "	-.0030 "	.1985 "	-.0015 "
.1985 "	-.0015 "	.1982 "	-.0018 "
.1983 "	-.0017 "	.1983 "	-.0017 "
.00074 Blank		.00074 Blank	
.1971 Average	-.0029 "	.1977 Average	-.0023 "

(b) Titrations in carbon dioxide.

Reduced 15 min.		Reduced 30 min.	
Tin found.	Error.	Tin found.	Error.
.1975 gram	-.0025 gram	.1984 gram	-.0016 gram
.1965 "	-.0035 "	.1984 "	-.0016 "
.1982 "	-.0018 "	.1987 "	-.0013 "
.1982 "	-.0018 "	.1982 "	-.0018 "
.1977 "	-.0023 "	.1984 "	-.0016 "
.1975 "	-.0025 "	.00076 Blank	
.00074 Blank			
.1976 Average	-.0024 "	.1984 Average	-.0016 "

TABLE VI.

Amount of hydrochloric acid in each sample 50 cc.

(a) Titrations in air.

Reduced 15 min.		Reduced 30 min.	
Tin found.	Error.	Tin found.	Error.
.1908 gram	-.0092 gram	.1946 gram	-.0054 gram
.1939 "	-.0061 "	.1947 "	-.0053 "
.1952 "	-.0048 "	.1947 "	-.0053 "
.1950 "	-.0050 "	.1960 "	-.0040 "
.1944 "	-.0056 "	.1948 "	-.0052 "
.0007 Blank		.0007 Blank	
.1939 Average	-.0061 "	.1949 Average	-.0051 "

(b) Titrations in carbon dioxide.

Reduced 15 min.		Reduced 30 min.	
Tin found.	Error.	Tin found.	Error.
.1957 gram	-.0043 gram	.1982 gram	-.0018 gram
.1947 "	-.0053 "	.1965 "	-.0035 "
.1965 "	-.0035 "	.1965 "	-.0035 "
.1957 "	-.0043 "	.1987 "	-.0013 "
		.1965 "	-.0035 "
.0007 Blank	______	.1957 "	-.0043 "
.1957 Average	-.0043 "	.0007 Blank	______
		.1972 Average	-.0028 "

TABLE VII.

Amount of hydrochloric acid in each sample 80 cc.

(a) Titrations in air.

Reduced 15 min.		Reduced 30 min.	
Tin found.	Error.	Tin found.	Error.
.1901 gram	-.0099 gram	.1941 gram	-.0059 gram
.1917 "	-.0083 "	.1939 "	-.0061 "
.1914 "	-.0086 "	.1941 "	-.0059 "
.1912 "	-.0088 "	.1927 "	-.0073 "
.1895 "	-.0105 "		
.0013 Blank	______	.0015 Blank	______
.1908 Average	-.0092 "	.1937 Average	-.0063 "

(b) Titrations in carbon dioxide.

Reduced 15 min.		Reduced 30 min.	
Tin found.	Error.	Tin found.	Error.
.1913 gram	-.0087 gram	.1945 gram	-.0055 gram
.1972 "	-.0028 "	.1938 "	-.0062 "
.1918 "	-.0082 "	.1976 "	-.0024 "
.1967 "	-.0033 "	.1981 "	-.0019 "
.1933 "	-.0067 "	.1970 "	-.0030 "
.1913 "	-.0087 "	.1976 "	-.0024 "
.1978 "	-.0022 "	.1978 "	-.0022 "
.0015 Blank		.0018 Blank	
.1942 Average	-.0058	.1966 Average	-.0034 "

(Summary of Tables V, VI, and VII on page 19.)

TABLE VIII.

Summary of Tables V, VI and VII, containing averages. The weights of tin in lines preceded by (a) were reduced for 15 minutes; those preceded by (b) for 30 minutes.

Table V, acid concentration 20 cc.

	Titrated in air.			Titrated in CO_2.			Increase
	Tin found.	Error.		Tin found.	Error.		due to CO_2.
(a)	.1971 gram	-.0029	---	.1976 gram	-.0024	---	.0005 gm
(b)	.1977 "	-.0023	---	.1984 "	-.0016	---	.0007 "
	Increase	.0006		Increase	.0008		

Table VI, acid concentration 50 cc .

	Titrated in air.			Titrated in CO_2.			Increase
	Tin found.	Error.		Tin found.	Error.		due to CO_2.
(a)	.1939 gram	-.0061	---	.1957 gram	-.0043	---	.0018 gm
(b)	.1949 "	-.0051	---	.1972 "	-.0028	---	.0023 "
	Increase	.0010		Increase	.0015		

Table VII, acid concentration 80 cc .

	Titrated in air.			Titrated in CO_2.			Increase
	Tin found.	Error.		Tin found.	Error.		due to CO_2.
(a)	.1908 gram	-.0092	---	.1942 gram	-.0058	--	.0034 gm
(b)	.1937 "	-.0063	---	.1966 "	-.0034	--	.0029 "
	Increase	.0029		Increase	.0024		

6. Tests with the atmospheric oxidation eliminated.

These tests were made with the Pearce-Low method to determine what percent of tin it would give when the air was excluded as much as possible with pure carbon dioxide during the reduction, cooling and titration. The introduction of air during the washing of the nickel coils was prevented by the use of nickel filings which were dissolved and did not require removal and washing. The carbon dioxide was made from pure sodium carbonate and hydrochloric acid in a Kipp generator. It was first passed through two Drexhel gas washing bottles containing a mixture of equal parts of concentrated hydrochloric acid and stannous chloride. The carbon dioxide was then passed through a third washing bottle containing concentrated hydrochloric acid. This served to prevent the possibility of the escape of stannous chloride with the carbon dioxide from the washing bottles, and also to prevent the weakening of the acid concentration in the flask used for the analysis. The carbon dioxide from the third washing bottle passed into an Erlenmeyer flask containing the solution of tin for the analysis. This flask was fitted with a three holed rubber stopper. The carbon dioxide passed out of this flask through a second hole of the stopper into a washing bottle containing a solution of sodium hydroxide. The third hole of the rubber stopper

was kept closed except when used for the introduction of the starch solution and for the tip of the burette during the titration.

For these tests a solution of stannic chloride was made as described on page 7 in the (2) Tests for completeness of reduction. Fifty cc of this solution containing .2 of a gram of tin was measured into a 500 cc Erlenmeyer flask. Enough concentrated hydrochloric acid was added to make a total of 50 cc of acid and the solution made up to a total volume of 200 cc with hot water. Six to seven tenths of a gram of fine nickel filings were then added and the flask tightly stoppered with the three holed rubber stopper connected as described above. The current of carbon dioxide was passed through the flask, rapidly at first and then more slowly during the remainder of the analysis. The flask was heated until the nickel filings had completely dissolved. (About 45 min.) The flame was then removed and the flask surrounded by a vessel of cold water. After the stannous solution had cooled starch solution was added through the third hole of the stopper and the hole stoppered with the tip of the burette. The stannous solution was then titrated in the usual way. The results of the analyses made in this way are given in Table IX.

The solutions analyzed in this way gave the entire amount of tin and agreed reasonably well. This shows that

the use of nickel filings and carbon dioxide as described above prevents the atmospheric oxidation which causes the low results obtained by the Pearce-Low method in the usual way.

TABLE IX.

Tests with the atmospheric oxidation eliminated.

Weight of tin in all solutions .2000 gram.

Acid concentration 50 cc HCl in total volume of 200cc.

Reductions with .6 to .7 gram of nickel filings.

No.	Iodine used.	Tin found.	Error.
1	39.30 cc	.2002 gram	+.0002 gram
2	39.15 "	.1995 "	-.0005 "
3	39.25 "	.2000 "	.0000 "
4	39.30 "	.2002 "	+.0002 "
5	39.30 "	.2002 "	+.0002 "
6	39.30 "	.2002 "	+.0002 "
7	.15 Blank	.0007 "	
8	.15 Blank	.0007 "	
	Average ---	.20006 "	+.00006 "

Same solution analyzed by the Pearce-Low directions.

Blank	.15 cc	.0007 gram	Error.
1	37.90 "	.1931 "	-.0069 gram
2	38.90 "	.1936 "	-.0064 "

.1791 gram SnO_2 analyzed as the 6 samples above

Required 27.65 cc of iodine, giving .1408 gram tin.

Error -.0003 "

IV. SUMMARY. The method described by Low and Pearce (Low's Ore Analysis p 208, 1908 Edition.) for analyzing tin ores does not give the entire amount of tin. The shortage of one to four percent is not due to incomplete solution of tin, incomplete reduction of stannic chloride or volatilization of stannic chloride, but is caused by atmospheric oxidation. This oxidation increases with the acid concentration and is partly prevented by the evolution of carbon dioxide from marble in the flask during cooling and titration. The atmospheric oxidation and the shortage in the amount of tin are entirely prevented when nickel filings are used for the reduction and the air excluded by passing pure carbon dioxide through the tightly stoppered flask used for the analysis of the tin solution.

APPROVED BY

Victor Lenher

April 28 1914

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